

Electron-electron interaction in multiwall carbon nanotubes[★]

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Abstract

Magnetic susceptibility χ of pristine and brominated arc-produced sample of multi-wall carbon nanotubes was measured from 4.2 to 400 K. An additional contribution $\Delta\chi(T)$ to diamagnetic susceptibility $\chi(T)$ of carbon nanotubes was found at $T < 50$ K for both samples. It is shown that $\Delta\chi(T)$ are dominated by quantum correction to χ for interaction electrons (interaction effects-IE). The IE shows a crossover from two-dimensional to three-dimensional at $B = 5.5$ T. The effective interaction between electrons for interior layers of nanotubes are repulsion and the electron-electron interaction λ_c was estimated to be $\lambda_c \sim 0.26$.

Key words: Electron-electron interaction; Carbon nanotubes; Magnetic susceptibility; Brominated carbon nanotubes.

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From the time of discovery nanotubes one of the most important problems is the possibility of a superconducting state in them. In a series of experiments were observed the effects which indicate on its existence. There is supercurrents through single-walled carbon nanotubes [1], persistent currents and magnetic flux trapping [2]. As is known the nature of a superconducting state is the electron-electron interaction (Namely - attraction between electrons). On the other hand electron-electron interaction is exhibited in electronic transport properties of conductors in normal state - so-called quantum interference effects - interaction effects (IE) [3,4]. IE are connected with the correction

[★] Expanded version ..

to density of states of conduction electrons in a results of quantum interferences of electrons at their diffuse motion in random conductors. But in such systems the one-particle processes, so-called weak localization (WL) [3] and weak antilocalization (WAL) [5], always accompany with IE.

The observation of IE corrections to χ is very important for partition of including of WL, WAL, and IE to different physical properties. From all these corrections only IE contributes to χ .

For observation of IE corrections to χ it is necessary to divide the contributions connecting with IE and much more on quantity a magnetic susceptibility of sample, and exclude the contribution of paramagnetic impurities. Only in separate cases it is possible. Earlier, with the using of relaxation processes in Mo_2S_3 [6], we changed the contribution connected with IE correction to χ by quenching of high-temperature metastable state of a sample. In a results, with the using of difference contribution to χ in equilibrium and metastable states, we received the IE correction to χ in the pure state [7]. In this work, with the using of chemical modification of a sample (brominated), we singled out IE correction to χ in laminated structures based on multi-layer carbon nanotubes (LS of MWNT).

The material which contained MWNTs was synthesized using a set-up for arc discharge graphite evaporation, which was described elsewhere [8,9]. The arc was maintained with a voltage of 35 V and a current of 1000 A for 15-20 minutes in helium atmosphere of 800 Torr. A nanotube content in the inner part of carbon deposit grown on the cathode was estimated by transmission electron microscopy to reach about 80% [10]. Tubes have from 2 to 30 shells with an outer diameter of 60-150 Å. Scanning electron microscopy (SEM) revealed a predominant orientation of MWNTs was perpendicular to the deposit growth axis (Fig. 1).

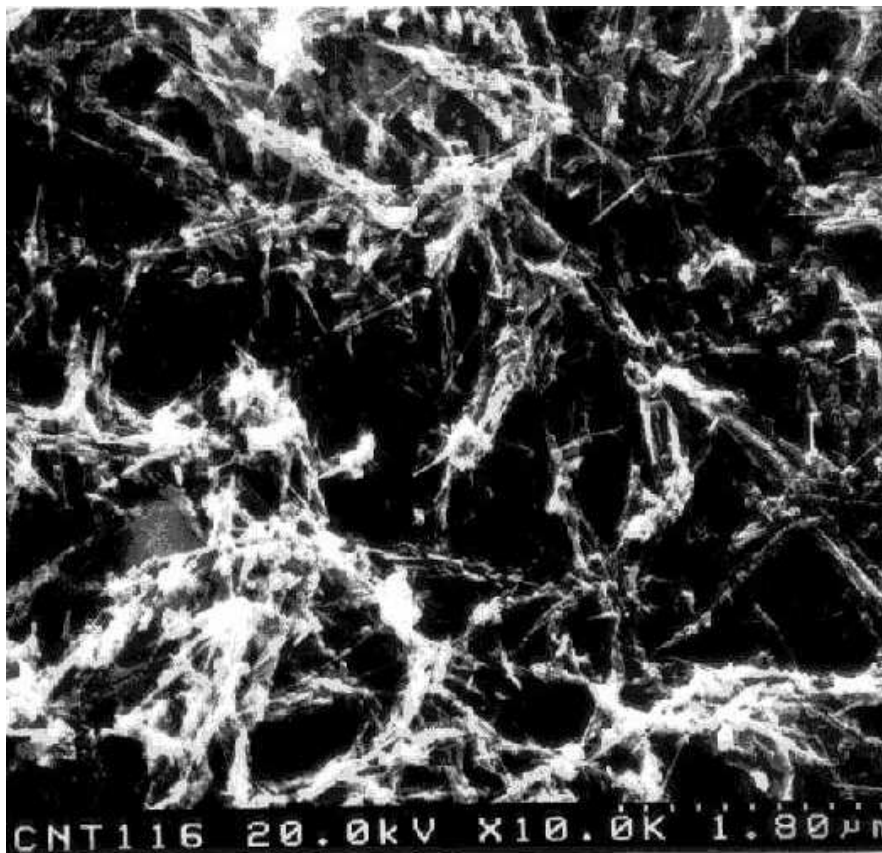


Fig. 1. The SEM micrograph of pristine macro-samples LS of MWNT. The deposit axis was perpendicular to picture.

The brominated material was prepared by exposure of the pristine one to Br_2 vapors during 7 days. Its composition $\text{CBr}_{0.06}$ was determined by x-ray photoelectron spectroscopy.

For magnetic measurements a cylindrical sample of diameter 5mm and of length 10 mm was cut out from the pristine or brominated material so that its axis was coincident with the deposit one. As a result, the magnetic field was perpendicular to most of carbon nanotubes in the sample. The weight of samples was about 0.3 grams. The temperature dependence of magnetic susceptibility χ for the samples was measured from 4.5 to 400 K in a field of 0.01, 0.5, and 5.5 T by using a model MPMS-5 SQUID (QUANTUM DESIGN, USA).

According to experimental and theoretical data, the basic contribution in χ of quasi-two-dimensional graphite (QTDG), including MWNTs, gives orbital magnetic Susceptibility χ_{or} connected with extrinsic carriers (EC) [11–13].

Figure 2(a) presents the magnetic susceptibility χ of pristine sample as a function of temperature. The observed behavior was similar to the previously

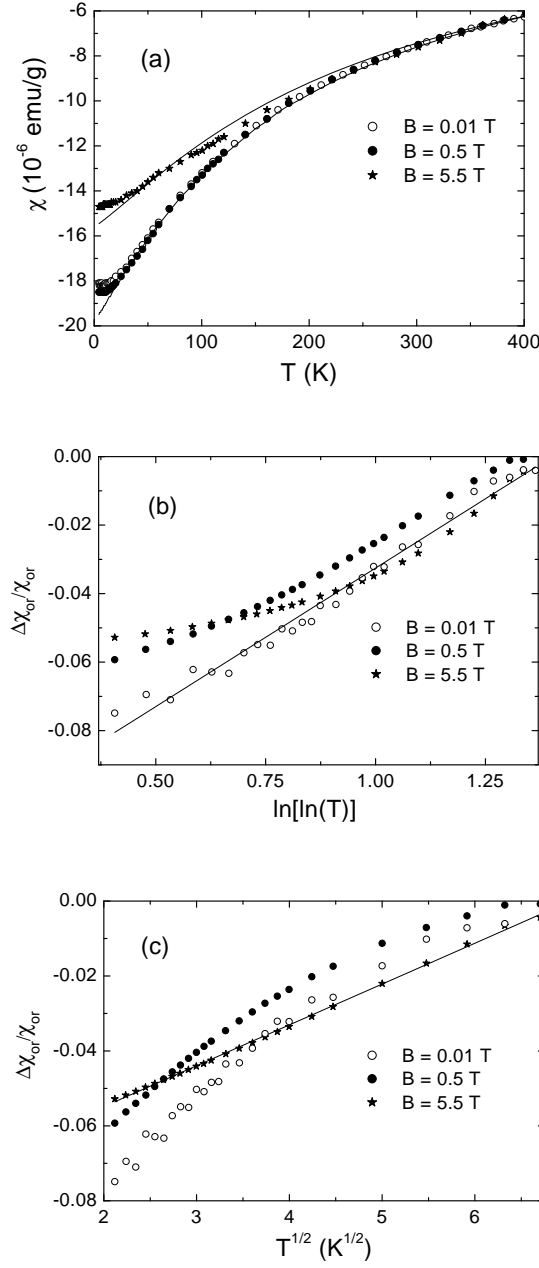


Fig. 2. The temperature dependence of magnetic susceptibility $\chi(T)$ (a) and $\Delta\chi_{or}(T)/\chi_{or}(T) = [\chi(T) - \chi_{or}(T)]/\chi_{or}(T)$ [(b) and (c)] for pristine sample. The solid lines are fits: for (a) by Eq. (1) in interval 50 - 400 K with parameters; for curve (○), $\gamma_0 = 1.6$ eV, $T_0 = 215$ K, $\delta = 159$ K; for (●), $\gamma_0 = 1.6$ eV, $T_0 = 215$ K, $\delta = 159$ K; for (★), $\gamma_0 = 1.7$ eV, $T_0 = 327$ K, $\delta = 210$ K; by Eq. (2) and Eq. (3) for (b) and (c) respectively in interval 4.5 - 45 K with parameters $T_c = 10000$ K, $l_{el}/a = 0.15$.

reported measurements on the samples of MWNTs [11–15].

Available models well reproduce the temperature dependence of magnetic susceptibility for MWNTs only at $T > 50$ K [11–13,16,17]. In the low-temperature region the experimental data deviate from the theoretical ones that are usually attributed to the paramagnetic impurities contribution. To analyze this anomalous part of the magnetic susceptibility χ in detail, that was a goal of the our work, it was necessary to select its high-temperature portion previously. According to theoretical consideration the magnetic susceptibility χ of quasi-two-dimensional graphite (QTDG) is generally contributed by two components: diamagnetic susceptibility χ_D [11–13,16,17] and paramagnetic spin susceptibility χ_s . The amount of metallic impurities in the samples under investigation was detected by spectrographic analysis and was less than 10^{-5} . Furthermore, the signal corresponding to the unpaired spins of transition metals was absent in the EPS spectrum of samples (detection limit equal to 10^{-6}). Thus the paramagnetic spin contribution to the magnetic susceptibility χ of the measured materials was negligible. Hence, the χ of MWNT sample have been determined by the component χ_D [11]

$$\chi_{or}(T) = -\frac{5.45 \times 10^{-3} \gamma_0^2}{(T + \delta)[2 + \exp(\eta) + \exp(-\eta)]}, \quad (1)$$

where γ_0 is the band parameter for two-dimensional case, δ is the additional temperature formally taking into account "smearing" the density of states due to electron nonthermal scattering by structure defects, $\eta = E_F/k_B(T + \delta)$ represents reduced Fermi level (E_F), k_B is the Boltzmann constant. Using an electrical neutrality equation in the 2D graphite model [11] η can be derived by $\eta = \text{sgn}(\eta_0)[0.006\eta_0^4 - 0.0958\eta_0^3 + 0.532\eta_0^2 - 0.08\eta_0]$ [12] with an accuracy no less than 1%. The η_0 is determined by $\eta_0 = T_0/(T + \delta)$, where T_0 being degeneracy temperature of extrinsic carriers (EC) depends on its concentration n_0 only. The value of δ can be estimated independently [13] as $\delta = \hbar/\pi k_B \tau_0$, where \hbar is the Planck constant, τ_0 is a relaxation time of the carrier nonthermally scattered by defects [13]. Generally, the number of EC in QTDG is equal to that of scattering centers and δ depends only on T_0 , i.e. $\delta = T_0/r$, where r is determined by scattering efficiency [12]. These parameters were chosen to give the best fit of the experimental data (Fig. 2a). At high field ($B > 1$ T) the magnetic susceptibility $\chi(T)$ decreases in all interval of temperature. In this field region the magnetic length [3,4] $l_B = (\hbar c/2eB)^{1/2}$ is much less than a tube length. Therefore, susceptibility probes only small local areas of the graphite plane, and is expected to be the geometrical averaged of that of rolled-up sheets of graphite. At low fields the magnetic length is larger than the dimension of most tubes in the sample, and this geometrical correction may be neglected [14].

The data in Fig. 2 show that at $T < 50$ K there is an additional contribution $\Delta\chi_{or}(T) = \chi(T) - \chi_{or}(T)$ to $\chi(T)$. According to theoretical calculations [3,4] only electron-electron interactions can contribute to magnetic susceptibility,

which may be divided into two parts. The first part $\Delta\chi_{or}$ comes from correction to orbital susceptibility χ_{or} . The other part $\Delta\chi_s$ is associated with the correction to spin susceptibility χ_s . The latter contribution is negligible because the carbonaceous material used in sample preparation was indicated by spectrographic analysis and these material contained very small amount of magnetic impurities (less than detection limit). The dominated part $\Delta\chi_{or}$, divided on χ_{or} , was described by [3,4]

$$\frac{\Delta\chi_{or}(T)}{\chi_{or}(T)} = -\frac{\frac{4}{3}(\frac{l_{el}}{h})\ln[\ln(\frac{T_c}{T})]}{\ln(\frac{k_B T_c \tau_{el}}{h})}, (d=2), \quad (2)$$

$$\frac{\Delta\chi_{or}(T)}{\chi_{or}(T)} = -\frac{2(\frac{\pi}{6})\xi(\frac{1}{2})(\frac{k_B T \tau_{el}}{h})^{1/2}}{\ln(\frac{T_c}{T})}, (d=3), \quad (3)$$

where value of $\xi(\frac{1}{2}) \sim 1$, l_{el} is the electron mean free path; τ_{el} represents the elastic relaxation time, which is about 10^{-13} sec for MWNT [18]; h is the thickness of layer in two-dimensional case; d denoted a system dimensionality; $T_c = \theta_D \exp(\lambda_c^{-1})$, where θ_D is the Debye temperature and λ_c is the constant described the electron-electron interaction in Cooper canal ($\lambda_c > 0$ in a case of electron repulsion). The dependence in Eq. (2) is determined by $\ln[\ln(\frac{T_c}{T})]$ term because at low temperature, in the disordered systems, τ_{el} is the temperature independent while all other terms are constants. The dependence in Eq. (3) is governed by $T^{1/2}$ term as $T_c \gg T$ and, therefore, $\ln(\frac{T_c}{T})$ is constant relative to $T^{1/2}$.

The additional contribution to $\chi(T)$ as a function of $\ln[\ln(\frac{T_c}{T})]$ and $T^{1/2}$ is presented in Fig. 2(b) and Fig. 2(c). The $\Delta\chi_{or}(T)/\chi_{or}(T)$ clearly shows the dependence given by Eq. (2) at low magnetic field and one given by Eq. (3) at high magnetic field, while at $B = 0.5$ T the temperature behavior of $\Delta\chi_{or}(T)/\chi_{or}(T)$ is deviated from these two cases. As seen from Fig. 2, an absolute value of $\Delta\chi_{or}(T)/\chi_{or}(T)$ at all magnetic fields applied to the pristine sample increases with decreasing temperature that has been predicted for IE in the systems characterized by electron-electron repulsion [3,4]. Hence, at $B = 5.5$ T a transfer from two-dimensional IE correction to three-dimensional one takes place. At lower magnetic field the interaction length $L_I(T) = (\hbar D/k_B T)^{1/2}$ is much less than the magnetic length $l_B = (\hbar c/2eB)^{1/2}$, which in turn becomes dominant at high field. An estimation of the characteristic lengths gave respectively the value of $L_I(4.2K) = 130$ Å (taking into account that the diffusion constant $D = 1$ cm²/s [18]) and the value of $l_B = 100$ Å at $B = 5.5$ T.

Taking into account experimentally apparent crossover (Fig. 2) from two-dimensional (equation 2) to three-dimensional (equation 3) of temperature dependence of $\Delta\chi_{or}(T)/\chi_{or}(T)$ we concluded that effective diameter of nanotubes was in an interval between 100 Å and 130 Å.

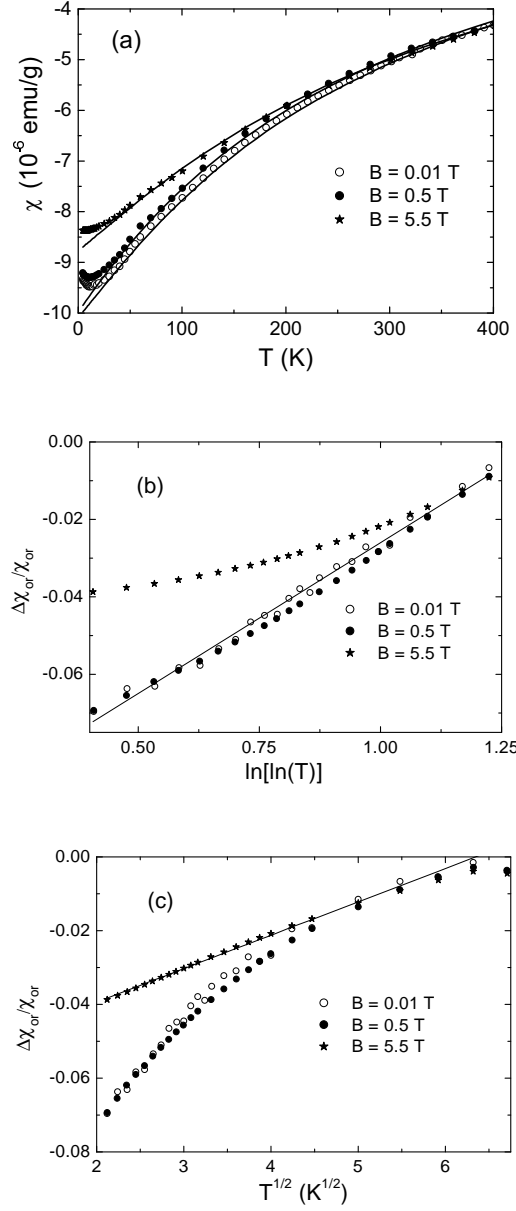


Fig. 3. The temperature dependence of magnetic susceptibility $\chi(T)$ (a) and $\Delta\chi_{or}(T)/\chi_{or}(T) = [\chi(T) - \chi_{or}(T)]/\chi_{or}(T)$ [(b) and (c)] for brominated sample. The solid lines are fits: for (a) by Eq. (1) in interval 50 - 400 K with parameters; for curve (○), $\gamma_0 = 1.4$ eV, $T_0 = 340$ K, $\delta = 252$ K; for (●), $\gamma_0 = 1.4$ eV, $T_0 = 300$ K, $\delta = 273$ K; for (★), $\gamma_0 = 1.5$ eV, $T_0 = 435$ K, $\delta = 325$ K; by Eq. (2) and Eq. (3) for (b) and (c) respectively in interval 4.5 - 45 K with parameters $T_c = 10000$ K, $l_{el}/a = 0.15$.

Partitioning of the contributions $\chi_{or}(T)$ and $\Delta\chi_{or}(T)/\chi_{or}(T)$ can be carried out in a result of changing of extrinsic carriers by the chemical modification of the pristine sample. In this case the $\chi_{or}(T)$ should be changed [11] and the $\Delta\chi_{or}(T)/\chi_{or}(T)$ remain the invariable [3,4].

The intercalation of single wall carbon nanotubes (SWNT) by bromine led to increase of n_0 [19]. We supposed that in MWNT may be similarly situation and used brominated MWNT for our investigations. Figure 3 show $\chi(T)$ for the brominated sample. The T_0 and δ for these sample are shown in figure 3 caption. We estimated n_0 at low temperature and low field in framework of theory of QTDG [13] $n_0 = 4(k_B T_0)^2 / (3\pi a^2 \gamma_0^2)$, where $a = 0.246$ nm - lattice parameter in layer. These estimations gives: $n_{0ini} \sim 3 \times 10^{10} \text{ cm}^{-2}$ - for pristine sample; $n_{0Br} \sim 10^{11} \text{ cm}^{-2}$ - for brominated sample. The n_0 increases in brominated sample about 3 times. According to the Drude formula, the conductivity is proportional to n_0 and τ_{el} . We measured the conductivity of pristine and brominated samples and find that conductivity increase in 3 times in a result of bromination. Taking into account that n_0 also increase by about 3 times in a result of bromination we conclude that τ_{el} practically did not change during bromination. The $\Delta\chi_{or}(T)/\chi_{or}(T)$ don't change during intercalation [Fig. 3(b) and Fig. 3(c)]. This result indicates that $\Delta\chi_{or}(T)/\chi_{or}(T)$ doesn't connected with n_0 , and connected with the IE correction to χ . From experimental data $\Delta\chi_{or}(4.5K)/\chi_{or}(4.5K) = 0.027$ for three-dimensional IE correction to χ we estimated the T_c from Eq. (3) and fined $T_c = 5 \times 10^4$ K. We estimated the λ_c from $T_c = \theta_D \exp(\lambda_c^{-1})$ with Debye temperature for carbon nanotubes [20] $\theta_D = 1000$ K and obtained $\lambda_c \sim 0.26$. From experimental data $\Delta\chi_{or}(4.5K)/\chi_{or}(4.5K) = 0.07$ for two-dimensional IE correction to χ we estimated the l_{el}/h from Eq. (2) and fined $l_{el}/h \sim 0.15$. If $h \sim d_m$ and $100 \text{ \AA} \leq d_m \leq 130 \text{ \AA}$ so $20 \text{ \AA} \leq l_{el} \leq 15 \text{ \AA}$. This estimation in a quite good agreement with estimation $l_{el} = (D\tau_{el})^{1/2} \sim 30 \text{ \AA}$ for so crude estimation.

In summary, we have investigated the additional contribution to temperature dependence of orbital magnetic susceptibility $\Delta\chi_{or}(T)/\chi_{or}(T)$ of lamination structure of multiwall carbon nanotubes at $T < 50$ K. It is shown that $\Delta\chi_{or}(T)/\chi_{or}(T)$ is connected with quantum correction to magnetic susceptibility for interaction electron. At low field this correction is two-dimensional. At $B = 5.5$ T was observed three-dimensional correction to magnetic susceptibility. This crossover from $2d$ to $3d$ behavior of $\Delta\chi_{or}(T)/\chi_{or}(T)$ is connected with decreasing of magnetic length up to value less then typical mean diameter of nanotubes. It is shown that brominated of samples lead to increasing of extrinsic carriers n_0 from $n_{0ini} \sim 3 \times 10^{10} \text{ cm}^{-2}$ for pristine sample up to $n_{0Br} \sim 10^{11} \text{ cm}^{-2}$ for brominated samples. But $\Delta\chi_{or}(T)/\chi_{or}(T)$ did not changed when n_0 increases, which is in full agreement with theoretical predictions. From $\Delta\chi_{or}(4.5K)/\chi_{or}(4.5K)$, we estimated the constant of electron-electron interaction $\lambda_c \sim 0.26$. This interaction is repulsion for interior layers, which give the domination contribution to $\Delta\chi_{or}(T)/\chi_{or}(T)$ as a integration value.

It is necessary to note, that the correction to a magnetic susceptibility observation by us, and, accordingly estimation of a constant of electron-electron interaction it is integrated values average on all stratum in structural nanotubes. Therefore the made conclusion about repulsion character of interaction

between electrons does not eliminate opportunity of an attraction between electrons in high layer nanotubes, which contribution in magnetic susceptibility is small in comparison with sum by the contribution of all remaining stratum of a tube.

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